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Miniaturized Thermoelectric Power Sources

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ABSTRACT

Advanced thermoelectric microdevices integrated into thermal management packages and low power, electrical power source systems are of interest for a variety of space and terrestrial applications. By making use of macroscopic film technology, microgenerators operating across relatively small temperature differences can be conceptualized for a variety of high heat flux or low heat flux heat source configurations. The miniaturization of state-of-the-art thermoelectric module technology based on Bi_2Te_3 alloys is limited due to mechanical and manufacturing constraints for thermoelement dimensions (100-200μm thick minimum) and number (100-200 legs maximum). We are developing novel thermoelectric microdevices combining high thermal conductivity substrate materials such as diamond or even silicon, thin film metallization and patterning technology, and electrochemical deposition of 10-50μm thick thermoelectric films. By shrinking the size of the thermoelements and increasing their number to several thousands in a single structure, these devices can generate high voltages even at low power outputs that are more compatible with electronic components. Miniature power systems taking advantage of waste heat sources or organic fuel heat sources and combined with energy storage devices for enhanced performance are particularly attractive for terrestrial applications. Some details about the fabrication of the miniature devices are described.

INTRODUCTION

Solid state thermoelectric generators covering a wide range of power outputs, from nanowatts to kilowatts, have demonstrated attractive characteristics such as long life, the absence of moving parts or emissions, low maintenance and high reliability. In spite of a large number of potential civilian and military applications, their use has been severely limited due to their relatively low energy conversion efficiency and high development costs. To broaden the field of thermoelectrics, higher performance devices and systems need to be developed. One approach to achieve this goal is the discovery and infusion of novel thermoelectric materials more efficient above room temperature than the current state-of-the-art Bi_2Te_3, PbTe or SiGe alloys. Recent results in several laboratories have successfully identified superior materials in several temperature ranges [1-3]. There is currently an effort to introduce some of these new compounds into simple unicouple configurations to demonstrate the increased conversion efficiency [4]. The impact of this approach on device performance is illustrated in Figure 1.

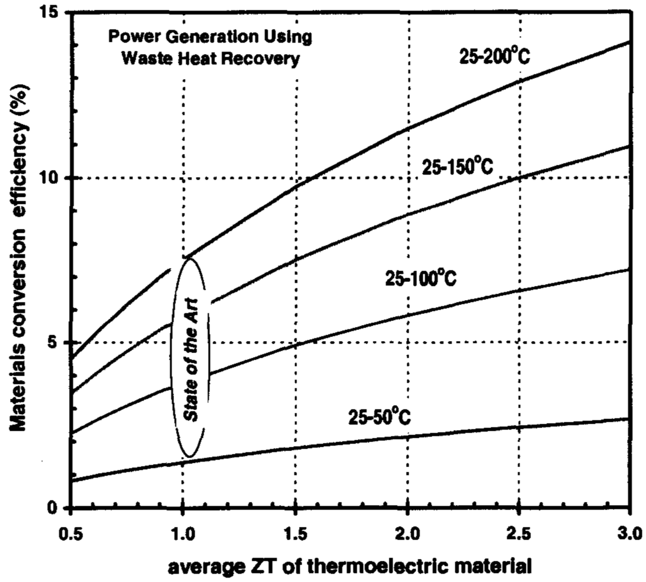

Figure 1: Improvement of thermoelectric generator performance when using more efficient materials. The temperature differences reported here are relevant to state-of-the-art Bi_2Te_3 alloys.

A second approach is to significantly improve the design, specific power (watts per unit area or volume) and lower the costs of generator devices even when using state-of-the-art thermoelectric materials. This is of great interest when considering large-scale applications using waste heat recovery schemes, or low power devices integrated with electronics and optoelectronics components. For both aerospace and terrestrial applications, there is a growing need for developing miniaturized on-chip low power batteries with long life, high voltage, resistance to extreme temperatures and low environmental impact characteristics [5, 6]. Current thermoelectric module technology is ill suited to such development due to mechanical and manufacturing constraints for thermoelement dimensions (100-200μm thick minimum) and number (100-200 legs maximum). In addition to the widespread use of semi-manual assembly techniques that results in high costs for more compact configurations, these devices have typically undesirable high current and low voltage characteristics. Much smaller devices capable of high voltage (up to 5V) power output in the nW to tens of μW range have also been developed: monolithic structures and more recently thin film devices. Most of the monolithic module configurations have been used in nuclear battery type devices, operating across large temperature differences (100-200K), with a small amount of radioisotope material (usually PuO_2) as the heat source [5, 7]. The specific power density of the monolithic thermopiles is typically measured in tens of mW/cm^3, but falls to about 60 μW/cm^3 when taking into account the complete power source package. Thin film devices producing 20 mW at 4V under load with a temperature difference of 20K have been recently described [8]. The ~~0.67x0.95x0.35~~ cm^3 device is comprised of 2250 thermocouples deposited on Kapton thin foils packed together and was fabricated using integrated circuit-type techniques. However, in spite of this remarkable achievement that could allow for batch fabrication of these devices, the specific power density still remains quite low, close to 90 μW/cm^3 (heat source not included). This is mainly due to the fact that the length of the thermoelectric legs is supported by the Kapton substrate, thus introducing a very significant thermal shunt and dramatically degrading conversion efficiency.

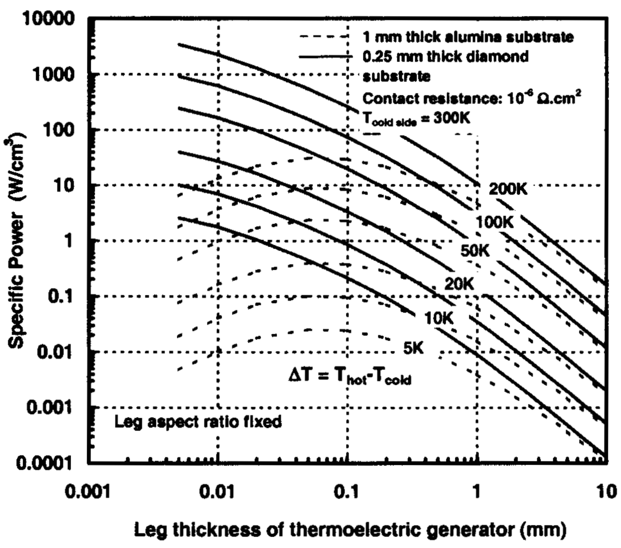

Figure 2: Calculated increase in specific power (per unit volume) with increasing leg miniaturization (constant cross section to length leg aspect ratio) and increasing temperature differences of operation. Data are shown for both low (alumina, blue dots) and high (diamond, red lines) thermal conductivity substrates.

MINIATURIZED GENERATOR DEVICES

To circumvent key shortcomings described in the preceding section, the Jet Propulsion Laboratory (JPL) is pursuing the development of vertically integrated thermoelectric microdevices that can be fabricated using a combination of thick film electrochemical (ECD) and integrated circuit (IC) processing techniques [9]. Indeed, current prototype devices leave much room for performance improvement, as illustrated in Figure 2. Even for relatively small temperature differences, such as 10 to 20K, high specific power outputs in the 1 to 10 W/cm^3 are potentially achievable provided that the legs be no thicker than 50 to100 μm.

MICRODEVICE CONFIGURATION

The term "vertically integrated" here refers to the conventional thermoelectric module configuration shown in Figure 3. This design eliminates the large heat losses observed in planar thin film thermoelectric devices where the legs are deposited onto a supporting substrate. However, planar configurations do offer a very convenient way of fabricating electrical interconnects between the thin film legs by using traditional masking techniques.

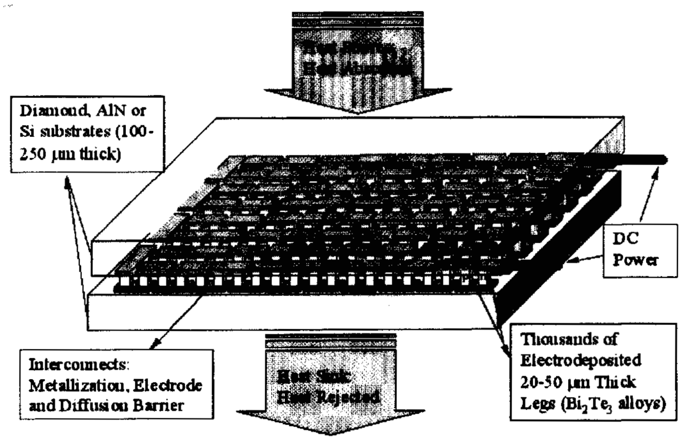

Figure 3: Schematic representation of a vertically integrated thick film thermoelectric generator using thin high thermal conductivity substrates.

Thermal resistances due to heat transfer through the metallizations and substrates, as well as electrical resistances due to the interconnects between n-type and p-type thermoelectric legs, rapidly become important issues when increasing device miniaturization. High thermal conductivity substrates, thin metallizations and intimate contact with the heat source and heat sink media are key to minimizing thermal issues when the microgenerators operate in particular under low temperature differences and high heat flux conditions. Since high voltage power output are highly desirable from a power conditioning aspect, this means that the microdevices will typically possess several thousands of very short thermocouples. Electrical contact resistances can thus easily become a very large fraction of the total internal device resistance. However, low values are routinely obtained in the electronic semiconductor industry and similar processing techniques have been developed here. Finally thermally stable diffusion barriers are needed to maintain the integrity of the multilayered stack of substrates, metallic interconnects and thermocouples. The effectiveness of amorphous transition metal nitride diffusion barriers for metallizations on diamond, AlN and thermally oxidized silicon substrates has been recently demonstrated [10].

MICRODEVICE FABRICATION

Electrodeposition

Hot side temperatures for microdevice applications that we are currently considering are 200 to 500K. $Bi_{2-x}Sb_xTe_{3-y}Se_y$ alloys are the state-of-the-art materials best suited to these temperatures of operation. Since the thickness of the legs selected in our various device concepts ranges from 10 to 60μm, we have actively pursued the development of an electrochemical thick film deposition process. ECD constitutes an inexpensive way to synthesize semiconducting films [11] and, depending on the current density used in deposition, the deposition rate can be varied widely, up to several tens of microns per hour. In addition, slight variations in the deposition potential or solution concentration may possibly be used to induce off-stoichiometric films, thus providing p- or n-type doping through stoichiometric deviation. The electrodeposition of thermoelectric materials has not been widely investigated [12, 13] and new experimental methods must be developed to obtain p-type and n-type $Bi_{2-x}Sb_xTe_{3-y}Se_y$ compositions which are optimal for thermoelectric power generation in the temperature range of interest. An additional advantage of ECD is that some of the interconnect layers necessary to the fabrication of these devices, such as Cu for the electrical path or Ni for the Cu diffusion barrier can also be deposited by using different aqueous solutions.

Depositions are typically run near room temperature using standard electrochemistry techniques: a three electrode cell with open beaker configuration but with separate vessels for the reference electrode (saturated calomel electrode, SCE) and the counter/working electrodes. A salt bridge is used to electrically connect the two beakers. The counter electrode consists of a fine Pt mesh while metallic foils or metallized high thermal conductivity substrates such as diamond, AlN or Si/SiO_2 were used for a working electrode. Solutions contained dissolved high purity elements (Bi, Sb, Te, Se) into an acidic aqueous medium, typically HNO_3 and deionized water (pH ~ 0). Concentration of the elements in the electrolyte was varied between 0.0001 and 0.01 M. In the case of Sb-rich p-type $Bi_{2-x}Sb_xTe_3$ films where 1.3<x<1.5, a chelating agent must be added to prevent the spontaneous precipitation of an insoluble oxide compound and raise its maximum solubility (about $8x10^{-4}$ M in 1 M HNO_3 aqueous solution). Both the electrodeposition and cyclic voltammetry measurements were carried out using mechanical solution stirring and a computer-controlled EG&G Princeton Potentiostat/ Galvanostat 273A. Experimental results have demonstrated that both n-type and p-type Bi_2Te_3 alloy films could be deposited with transport properties similar to those of bulk materials. Deposition rates typically range from 4 to 15μm/hour, depending on electrolyte concentrations in Bi, Sb, Te or Se and applied voltage. Deposition rates are typically slower for p-type films due to the chelating additives. More details have been reported elsewhere [9].

Integrated Circuit Processing Approach

Building on the availability of new thick photoresist commercial products, we have developed templates suitable to the electrochemical deposition of legs as thick as 70μm and as small as 6μm in diameter. Actually, it has been determined that to be able to tightly control the geometry of the legs and prevent "mushrooming" growth, electrodeposition must be conducted in equally thick photoresist templates. The thick positive photoresist template is patterned with deep square or round shaped holes that must be pre-aligned on top of metallic interconnects. Figures 4 and 5 illustrate the result of IC-type processing.

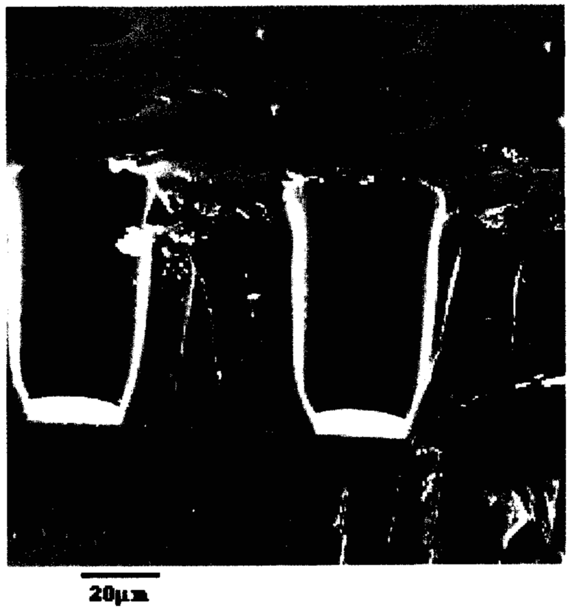

Figure 4: Thick positive photoresist template on top of a metallized Si/SiO_2 substrate. Deep cylindrical holes where the thermoelectric leg will be deposited can be seen.

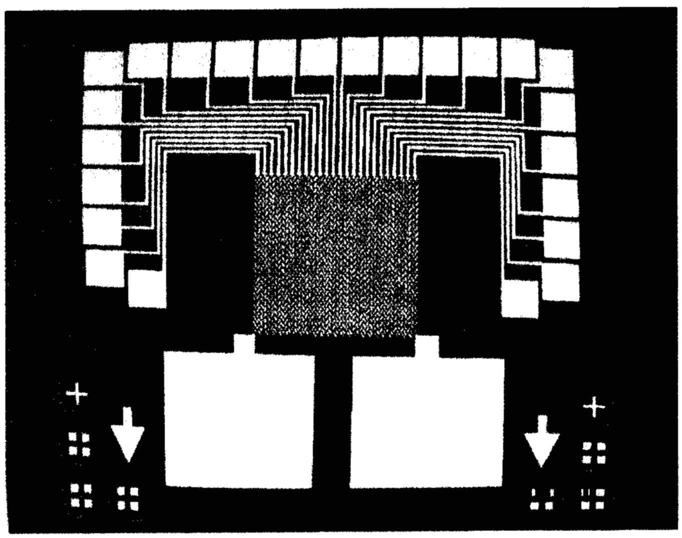

Figure 5: Cu metallization on top of a Si/SiO2 substrate where interconnects have been patterned for subsequent deposition of the thick photoresist template and thermoelectric legs. The fully metallized square pads are for providing electrical contact tests.

More processing steps are required to successively deposit n-type and p-type legs on top of the bottom substrate interconnects, and then ensure proper joining to a top substrate with similarly patterned electrical interconnects. Based on commercial electrolytes, we have used ECD techniques to deposit high quality Cu, Ni and Pb-Sn solder layers as well. The Pb-Sn layer can be used to form solder bumps on top of the legs, as done for flip-chip bonding techniques [14]. These processing steps are illustrated in Figure 6. The combination of ECD and IC-type techniques offer a degree of flexibility in designing and fabricating thermoelectric microdevices. It is interesting to note that typically a single photolithography mask can combine all of the necessary patterns to completely fabricate one generator configuration.

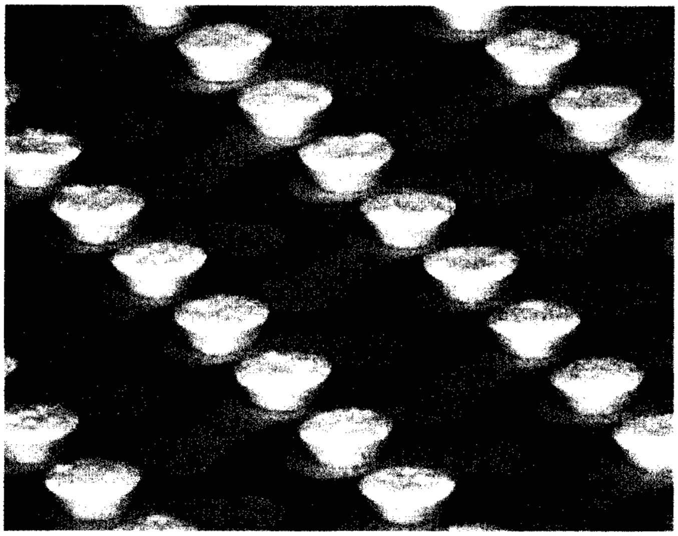

Figure 6: Bi_2Te_3 legs electrodeposited on top of Cu interconnect metallizations (using a Si/SiO_2 substrate).

THERMOELECTRIC MICROGENERATORS FOR "ENERGY HARVESTING' APPLICATIONS

To better illustrate possible applications of such highly miniaturized thermoelectric generators, let us consider an "energy harvesting" scheme where an environmental heat source is used to provide electrical power to operate electronic components in remote or unattended locations. One potential compact power source configuration is represented in Figure 7 where a microgenerator makes use of the temperature difference between air and soil temperatures. The microgenerator is used to trickle charge a set of rechargeable batteries or capacitors so that the hybrid power source can deliver a much higher power level for brief periods of time. Electronic measurement or communication devices coupled to the power source are thus allowed to operate following some nominal duty cycle. In this energy-harvesting scheme, thanks to the expected reliability of the thermoelectric microgenerator, the electronics will be operational for as long as sufficient air/soil temperature differentials exist and the energy storage components can handle the charge/discharge cycles.

This hybrid system consists of a small **6x6** cm^2 aluminum box covered with two layers of fins that is located at the surface while the heat is transferred to the soil by means of a 30cm long heat pipe terminated by a small spherical or cylindrical heat exchanger. Preliminary design operating conditions only require a low wind speed of 0.75m/s and air and soil temperatures of respectively 300K and 287K. Calculations show that the effective temperature difference across the thermoelectric microgenerator would be only 8.5K, but would be sufficient to produce about 22mW of power at 4.1V under resistive load. The microgenerator configuration is a set of 2300 n-type and p-type leg couples 50µm in thickness. The specific power performance of the device under such operating conditions is about 1.3W/cm^3 with a conversion efficiency of 0.4%.

However, temperatures will fluctuate during the day and at night the temperature profile will be reversed as the air becomes colder than the soil. As long as a temperature differential will be maintained across the thermoelectric microdevice, power will be generated. Power conditioning electronics are needed to handle the variations in output power, voltage and current over time and ensure proper charging and discharging of the energy storage components. Based on the design operating conditions described here, we estimate that the hybrid power source could deliver 100mW following a 10% duty cycle.

The first experimental characterization of the performance of various vertically integrated microgenerator devices will be carried out in the very near future at JPL as final assembly steps are now being developed. Results will be reported in later publications. If successful, we expect that this approach could be applied to a number of heat sources with different temperature ranges (such as combustion processes) and for a variety of power levels.

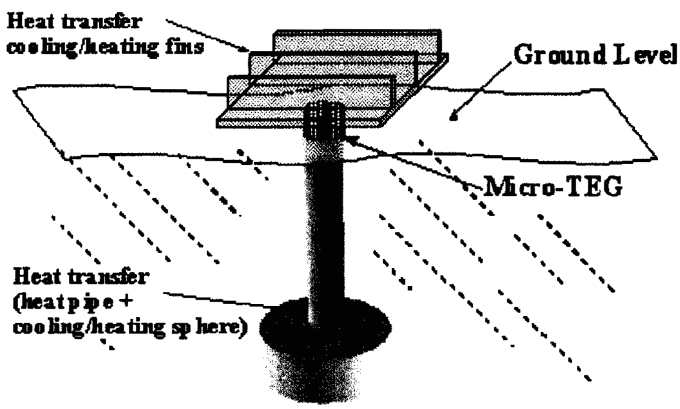

Figure 7: Schematic representation of an environmental energy harvesting power source concept that could be used to operate low power electronic components and eliminate the need for conventional batteries.

CONCLUSION

Thermoelectric microgenerators offer attractive solutions with high specific power output characteristics when considering low power electrical sources for remote or unattended electronics. However, thermoelectric technology to date is limited to bulky configurations based on monolithic thermopiles or to inefficient planar thin film devices. To fabricate better performing microdevices in a "classic" vertically integrated module configuration, a combination of electrochemical deposition techniques and integrated circuit technology is now under development. We have successfully electrodeposited both n-type and p-type thick Bi_2Te_3 alloy films (10-60 μm thick) from aqueous solutions and we have shown that transport properties similar to that of bulk materials can be achieved. Thermally stable metallizations to high thermal conductivity substrates and effective diffusion barriers for fabricating the electrical interconnects between the n- and p-type legs have also been demonstrated. Thick photoresist templates up to 70 μm have been successfully developed and patterned using conventional UV photolithography, resulting in the reproducible fabrication of highly packed arrays of thousands of legs as small as 6μm in diameter. We are now focusing on the fabrication of operational prototype devices with high specific power, high voltage characteristics that in particular can make use of environmental thermal energy harvesting schemes.

ACKNOWLEDGMENTS

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